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DEPARTMENT OF THE ARMY
Fort Detrick
Frederick, Maryland

THE SWELLING OF ACTIVATED CHARCOAL

P.N. Pawlow (Odessa)

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Translated by

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A. From the excellent research of Dora Schmidt-Walter¹ it is known

(1) Dora Schmidt-Walter, Koll.-Zeitschr. 14, 242 (1914).

that activated charcoal adsorbs acetic acid from solutions in benzene and toluene in accord with a curve that has a maximum and a minimum. The relationship between the adsorption and swelling isotherms for hide and cellulose, which also show maxima and minima on the curves, was established by the writer.² This led the writer to the opinion that the shape of the

(2) P.N. Pawlow, Koll.-Zeitschr. 40, 73 (1926).

adsorption curve of Dora Schmidt-Walter was also related to the shape of the swelling curve. In the present paper experiments are discussed which were based on a study of the capacity of charcoals to swell in pure solvents and solutions.

B. The magnitude of the swelling was measured using the volumetric method with test tubes 7-8 mm. diameter and 15 cm. long. By careful calibration a group of test tubes with equal diameters were assembled. The lower part of the test tubes were specially calibrated to the level of the proposed height of the charcoal mass. The fastest and most convenient method of removing the air occluded in the charcoal was as follows:

A weighed quantity was distributed over the inside walls of the test tube and, with the tube inclined, the liquid was poured in very slowly in an

attempt to wet the charcoal layer lying against the glass. Five cc. of liquid were poured in each time. After the liquid had infused, the test tube was held upright and the small bubbles of air were expelled by tapping the bottom and the sides with the fingers. The test tubes were tightly corked and energetically shaken to break up any small lumps of charcoal. Then the charcoal mass was stirred by air bubbles and the repeated rotation of the tubes. After the air had been removed the tightly corked test tubes were allowed to stand undisturbed. The escape of air from the charcoal sometimes continued for several days. A very convenient method for the removal of small air bubbles from the charcoal mass was, in addition to tapping the bottom of the tube, the rapid rotation of the test tube to left and right about the vertical axis. Tapping with the fingers on the bottom of the test tube for the purpose of control should not be discontinued while the infusion of the charcoal is continued, in order that the complete removal of the air from the swollen mass occurs. The height of the charcoal column was measured at chosen time intervals, usually daily. As the column became shorter with time and its height during the first hours after shaking was dependent in large measure on the sedimentation rate of the particles, the measurement was not made until one day later. The charcoal particles adhering to the stopper and the upper part of the test tube were washed down with liquid, after the charcoal mass had settled a little. The agitation and subsequent measurement of the height was repeated several times until finally only the reproducible heights were recorded. In order to determine a swelling curve, a series of test tubes was set up simultaneously. The room temperature at which the experiment was carried out was 13-15°C. and the following types of charcoal were used:

1. Graphite, Kahlbaum preparation, which was pulverized in a small electrically driven agate mill,
 2. Kahlbaum cane sugar charcoal,
 3. Kahlbaum animal charcoal, and
 4. K and K (Militärmedikamentendirektion) animal charcoal.
- This will be referred to as Animal charcoal A.

I. Swelling of Charcoal in Benzene and Toluene Solutions of Acetic Acid

1. The results of the charcoal swelling are given in Table I and Figure 1.

Table I

0.2 gm. animal charcoal A benzene + acetic acid		0.5 gm. cane sugar charcoal benzene + acetic acid		0.3 gm. animal charcoal A toluene + acetic acid	
Percent AcOH in 100gm. mixture	Height of char. column in mm. after 96 hrs.	Percent AcOH in 100gm. mixture	Height of char. column in mm. after 168 hrs.	Percent AcOH in 100gm. mixture	Height of char. column in mm. after 144 hrs.
0	44	0	33	0	58
0.3	47	0.3	37	0.24	67
2	40	2	36	0.48	64
5	36	5	32	0.9	60
45	33	6	31	10	52
60	32	30	29	20	50
70	32	45	28	35	49
80	32.2	70	27	50	47
90	32.7	90	26.5	70	45
100	33	100	26	80	47
				95	47.5
				100	50

The magnitude of the swelling of the charcoal in these solutions appeared as a function of the acid concentration. Animal charcoal A had a swelling maximum and minimum in both benzene and toluene solution. Swelling maxima were seen at very small acetic acid concentrations. The swelling of the cane sugar charcoal was considerably smaller than that of the animal charcoal. The time intervals in the table indicate the time of the last reading after the last agitation.

II. Swelling of Charcoal in Aqueous Acid and Alkali Solution

1. The Kahlbaum animal charcoal has been tested for swelling in acetic acid and sodium hydroxide solutions. The results are given in Table II and Figure 2.

Table II

0.4 gm. Kahlbaum animal charcoal

Water + acetic acid		Water + sodium hydroxide	
Percent AcOH in 100 gm. mixture	Height of char. column in mm. after 168 hrs.	Normality of NaOH solution	Height of char. column in mm. after 168 hrs.
0	66	0	66
0.02	66	N/1000	66
2	61	N/600	65
6	59	N/400	64
100	45	N/200	62
		N/50	55
		N/10	56.5
		6N/10	57
		1N	58

In addition to the acetic acid concentrations given in the foregoing table, others between 0.02 and 2 percent were examined in the hope that a swelling maximum and minimum might be found. At a concentration

of about 0.1 percent a swelling minimum was indicated which however could not be fixed conclusively because of a lack of charcoal and accordingly the concentration could not be established definitely. In the alkali medium a distinct swelling minimum can be seen at an initial concentration of N/50.

2. The cane sugar charcoal was also investigated in acetic acid and sodium hydroxide solutions. The results are given in Table III and Figure 2.

Table III

0.7 gm. cane sugar charcoal

Water + acetic acid		Water + sodium hydroxide	
Percent AcOH in 100 gm. mixture	Height of char. column in mm. after 120 hrs.	Normality of NaOH solution	Height of char. column in mm. after 120 hrs.
0	37	0	37
0.1	36.5	N/600	37
0.2	35.5	N/200	36
0.33	35.3	N/50	35.5
2	34	N/10	35.5
6	33.5	6N/10	37
16.8	32	1N	38
40	32		
80	32		
90	32		
100	32		

The swelling of the cane sugar charcoal was very much less than that of the animal charcoal. This also showed two minima: the one found in the alkaline medium at an initial concentration between N/50 and N/10 and the other in acid medium in the region of an initial concentration below 0.1 percent. The latter minimum was specially studied and will be described further in the following section.

3. The third type of charcoal - the strongly swelling Animal charcoal A - was also investigated in acetic acid and sodium hydroxide solutions. The results in acid solutions are given in Table IV and Figure 2.

Table IV

0.2 gm. Animal charcoal A

<u>Percent AcOH in</u> <u>100 gm. mixture</u>	<u>Height of char. column</u> <u>in mm. after 240 hrs.</u>
0	45
0.1	59
0.4	55
2	39
6	38
12	36
26	36
40	35
60	34
80	34
90	34
100	33

In addition to the concentrations listed in Table IV, 0.033 and 0.05 percent solutions were also studied. In these two solutions, just as in pure water, the charcoal formed no sediment at the bottom of the test tube, but accumulated in the upper part of the liquid-like cork. In the 0.1 and 0.4 percent solutions the charcoal remained in the upper part of the test tube for several days and only after a very long interval formed a sediment. In the table the height indicated was obtained after ten days when the charcoal had begun to settle to the bottom. In the two percent and stronger solutions the charcoal settled following infusion and light shaking. The height noted in pure water (45 mm.) was thickness of the charcoal floating

in the upper part of the test tube. With the 0.033 and 0.05 percent concentrations the thickness of the floating charcoal was considerably greater than 45 mm.

As the table shows the swelling curve of animal charcoal A has a maximum at a very small concentration of acetic acid. The experiment to measure the swelling minimum and the isoelectric point gave no definitive results in dilute solutions because of the upward streaming of the charcoal.

In sodium hydroxide solutions the animal charcoal A did not settle completely: in the N/600 and N/200 solutions the total quantity accumulated in the upper part of the liquid, while in the N/200, N/50, N/10 and N/1 solutions a part of the material was on the bottom and the rest at the top like cork. The swelling curve in alkali solution apparently also had a maximum.

III. The Isoelectric Point of Activated Charcoal

1. Two methods were used to determine the isoelectric point of the charcoal: (a) The pH of the solution was determined after a reversal of the direction of electroendosmosis³ (or electrophoresis), and (b) The pH

(3) Leonor Michaelis, Die Wasserstoffionenkonzentration, T.I., 224 (1922).

of the solution was measured, the magnitude of which was not altered by the treatment with charcoal.⁴

(4) Hans Eohn, Biochem. Zeitschr. 178, H. 1/3, 119 (1926).

The swelling capacity of charcoal found by the writer showed the possibility of the application of a third method, which is usually used with swelling gels, and assumes that the isoelectric point occurs at the same solution pH as gives a minimum of swelling of the charcoal.

In the preceding section reference was made to the fact that animal charcoal and Kahlbaum cane sugar charcoal showed two isoelectric points, one in acid and the other in alkali solution.

With animal charcoal only the alkali point was determined at an initial concentration of N/50. If the adsorption of the hydroxyl radicals was considered, a pH of 12-12.5 was obtained in the solution in contact with the charcoal. The acid point could not be determined accurately because of the lack of material.

2. With cane sugar charcoal both points were determined more or less accurately. In alkaline medium the isoelectric point was reached at a N/50-N/10 concentration of the initial solution. For a solution which had the charcoal in equilibrium the pH appears equal to 12-12.5. Thus the isoelectric points of animal charcoal and cane sugar charcoal were coincidental or nearly so.

Preliminary experiments in acid medium indicated the presence of an isoelectric point in solutions under 0.1 percent. Systematic experiments were undertaken with a buffer solution consisting of acetic acid and sodium acetate. N/10 acetic acid and N/10 sodium acetate were used as the starting solutions. The combinations of the solutions and the magnitudes of swelling in them are given in Table V.

0.8 gm. charcoal was placed in a very carefully calibrated test tube and moistened with 5 cc. of a suitable mixture. The liberation of small air bubbles on account of the large quantity of charcoal in the narrow test tube was carried out for several days by tapping and turning the tube. With the gradual disappearance of the gas evolution the picture of the minimum and maximum of the swelling became ever clearer. After the evolution had ceased (about four days after charging), the contents of the test tube were again shaken hard and the charcoal allowed to stand to settle quietly.

Table V

0.8 gm. cane sugar charcoal + 5 cc. solution

No. of soln.	Composition of solution (cc.)			Height of char. column in mm. after 120 hrs.	pH of final soln.
	H ₂ O	N/10 AcOH	N/10 AcONa		
1	5	0	0	43	
2	8.75	0.25	1	42.5	
3	8.5	0.5	1	41	
4	8	1	1	40.5 Minimum	8.3
5	7	2	1	41	
6	5	4	1	41.5	
7	1	8	1	42	
8	9	1	0	43	
9	8	2	0	43.5	
10	0	5	0	42	

It can be seen in Table V that the swelling minimum occurred with Solution No. 4. In this case the test tube contained too small a quantity of liquid for a pH determination, so this was done in a special adsorption experiment. Eight grams of charcoal were shaken in a small flask and moistened with 50 cc. of Solution No. 4. After shaking the contents, the flask was held at 11-12°C. for 120 hours. The liquid was put through a paper filter and the first portion of the filtrate discarded. The pH values for both the starting solution (No. 4) and the final solution were determined electrometrically. pH^{min} starting solution = 4.8; the isoelectric point, i.e. pH^{min} final solution = 8.3.

IV. Swelling of Graphite

1. In order to understand the reason for the swelling of activated charcoal, experiments were carried out to determine the behaviour of graphite and quartz powders in different solvents and solutions. Graphite, Kahlbaum preparation, was used for the experiments after being finely ground in a small electrically driven agate mill and sieved. The experimental procedure was the same as for charcoal. The experimental results in pure solvents are given in Table VI.

Table VI

1 gm. graphite + 5 cc. liquid

Solvent	Height of grph. column in mm. after 240 hrs.	Spec. grav. of liquids at 20° (d)	Molar vol. of liquids at 20°	Viscosity at 20° η	$\frac{d_{\text{graphite}} - d}{\eta}$
Acetic acid	32	1.0491	57.2	0.01222	100.7
Water	33	0.99823	18.0	0.0101	126.9
Ethyl acetate	34	0.9005	97.8	0.004546	303.5
Benzene	38	0.879	88.8	0.006537	214.3
Toluene	37	0.8659	106.3	0.005903	239.6
m-Xylene	31	0.8642	122.8	0.0062	228.4
Carbon tetrachlorid-		1.5939	96.5	0.00975	70.4
Graphite		2.28	--	--	--

Table VII is given for purposes of comparison and contains the behaviour of the charcoals in different solvents.

Table VII

		AcOH	H ₂ O	AcOEt	C ₆ H ₆	C ₇ H ₈	m-C ₈ H ₁₀	CCl ₄
1. Cane sugar	(0.5 gm.)	26	29	29.5	33	34	29	39
2. Animal A	(0.2 gm.)	33	--	--	44	44	--	--
3. Animal Kahlbaum	(0.2 gm.)	23	33	--	--	--	--	--

It can be seen in the tables that the degree of swelling of charcoal and graphite depended on the nature of the solvent and also that in terms of the intensity of the effect on charcoal and graphite the solvents can be arranged in an order corresponding to their increasing effect, which is as follows: Acetic acid < water < ethyl acetate < benzene = toluene = xylene < carbon tetrachloride. Graphite only differed from charcoal in having less swelling.

2. After the determination of this relationship, it was of importance to recognize the factors which force a given mass of graphite to settle in columns of differing heights in different liquids. It was first considered that the specific gravity, which determines the amount of the loss of the powder in relation to its weight, could serve as such a factor. However, in this case the height of the graphite column and the specific gravity of the liquid must be directly related quantities, i.e. with an increase of the specific gravity the height of a column of graphite powder must increase. It is evident from Table VI that no parallel existed between these values. Rather it was reversed; if carbon tetrachloride was excluded, then an inverse ratio was indicated. Consequently, the loss in weight of the volume and the height of the given mass of powder were not determining factors. The height of the column also did not depend on the settling rate of the particles. The expression $\frac{d_{\text{graphite}} - d}{\eta}$ was a measure of this velocity; but no simple relation existed between this value and the column height, as can be seen from Table VI.

Objection could also be raised to the consideration that the increase of the volume of the graphite mass took place because of the penetration of the solvent into the interior of the graphite particles, since the crystal lattice of graphite is impervious to gases and liquids.

The only remaining assumption was that the change of the powder volume was caused by the formation of a liquid layer on the surface of the pulverized mass and that the thickness of this layer depended on the nature of the liquid. If the liquid film building up on the graphite particles consisted of a layer of adsorbed liquid molecules, then the height of the powder in different liquids would be directly related to the molecular volumes of the liquids. However, as Table VI shows, no relationship actually existed between the molecular volumes and the level of the graphite mass.

Therefore it was assumed that the formation of the liquid layer on the graphite particles was the result of an electrical physical chemical force, which was directed from the molecules or atoms of the graphite to the solvent molecules and hence the surface of the powder was covered with a adsorbed-solvated layer. If it was assumed that a given quantity of pulverized graphite has a different volume in different liquids on account of surface solvation, then the possibility existed of using the designation swelling for the described phenomenon. In the degree of swelling there was a measure of the magnitude of the surface solvation.

The strong swelling of the graphite mass in benzene and its derivatives was remarkable. This was plausible since the structure of the crystalline graphite lattice had the valences ordered in the same way as the benzene nucleus. Consequently in this case a large adsorption-solvation by affinitive substances on its structure was obtained.

V. Swelling of Quartz and Ferric Hydroxide

1. In order to prove that the surface solvation of graphite was not an exceptional phenomenon but the general behaviour of pulverized solids

in contact with different solvents and solutions, experiments were carried out on the swelling of different insoluble materials. The experiments on quartz and ferric hydroxide are described in this section. For the quartz experiments Quartz Kahlbaum was calcined and pulverized. The results obtained in different solvents are shown in Table VIII.

Table VIII

1.2 gm. quartz + 5 cc. liquid

	<u>H₂O</u>	<u>AcOH</u>	<u>AcOEt</u>	<u>C₇H₈</u>	<u>m-C₈H₁₀</u>	<u>CCl₄</u>
Height in mm.	20	26	32	52	51	70

In water and weak acetic acid solutions a strong turbidity occurred after shaking which disappeared after 3-4 days. In water, acetic acid and ethyl acetate the quartz remained as a pulverized white mass; in carbon tetrachloride it formed an art gallery of opal-like tones; gallery-like colours occurred also in toluene and m-xylene.

2. Ferric hydroxide was prepared by the action of ammonium hydroxide on ferric chloride and was freed of ammonium chloride by repeated decantation and settling. The ferric hydroxide was considered ready for experimental use when the wash water only showed a slight opalescence with silver nitrate. The ferric hydroxide gel had different heights in solutions of sodium hydroxide of different concentrations. In very weak solutions the gel height went through a maximum and a minimum and in stronger solutions maintained a constant value. Since the peculiar phenomena which were observed will be described in a special paper, this section will be limited to the bare establishment of these facts.

3. The swelling phenomena of finely divided materials which have been discussed in this and foregoing sections depend on surface solvation, that is on the accumulation of the solvent on the surface of the material submerged in it under the influence of an electrical physical chemical reciprocal force between the body of the solvent and that of the pulverized material. This surface build-up can only be considered as the result of the adsorption of the solvent by the fine granular phase. The swelling phenomena of the fine granular materials described here are clear proof of solvent adsorption on the surface which has been assumed by many investigators from the works of A.M. Williams⁵ and Wo. Ostwald⁶ and which was taken as the

(5) A.M. Williams, Medd. Nobelinstitut 2, No. 27 (1913).

(6) Wo. Ostwald, Koll.-Zeitschr. 30, 279 (1922).

basis of his thermodynamic investigation of capillary adsorption by the writer.⁷

(7) P.N. Pawlow, Koll.-Zeitschr. 35, 89 (1924).

VI. Swelling of Charcoal and Its Activity

1. As is known different types of charcoal possess unequal adsorptive capacities towards dissolved substances. Correspondingly the charcoals were differentiated by their activity. With the small charcoal assortment that was available the relationship between the adsorption activity of the charcoals and their capability of swelling was investigated. Strong swelling in pure water characterized the most active types of charcoal. Charcoal swollen in water had a larger volume than a similar weight of charcoal in air. The magnitude of the swelling was characterized by the magnitude of relative swelling. If h_0 was the height of the charcoal column in a test tube in air and h the height of the same weight of charcoal in the test tube in water,

then $\frac{h - h_0}{h_0}$ was the relative swelling. For each type of charcoal the magnitude of the relative swelling was a constant.

In order to measure the quantity h_0 the test tube with the charcoal in it was tapped on an elastic cork slab until the height of the charcoal column no longer changed. The resultant height was recorded as h_0 . Then the charcoal mass was spread along the side of the tube and, as described previously, moistened with 5 cc. of distilled water. The test tube was not shaken afterwards to prevent any charcoal particles being lost through adhesion to the stopper; the small air bubbles were worked out by tapping the test tube on the cork slab. The height of the charcoal column h in the test tube with water was usually observed for several days in order to determine the constant value. In Table IX the results of measurements on two types of charcoal are given.

Table IX

0.33 gm. charcoal + 5 cc. distilled water

<u>Type of charcoal</u>	<u>h_0</u>	<u>h</u>	<u>$\frac{h - h_0}{h_0}$</u>
1. Animal charcoal Kahlbaum	23.5	35	0.489
2. Cane sugar charcoal Kahlbaum	14.5	16	0.103

The relative swelling of the animal charcoal was larger than that of the cane sugar charcoal. The animal charcoal also had a larger adsorptive capacity than the cane sugar charcoal.

2. The swelling curve and the curve of the apparent adsorption for charcoals were probably related in the same way as the writer's observations have indicated for hide and cellulose. In order to complete the investigation a proofing test with several acetic acid concentrations was undertaken to

determine the dependence between the magnitude of the apparent adsorption and the relative swelling in solution. Table X shows the experimental results for an acetic acid concentration of N/1.821. This solution was used for observations both of the swelling and the adsorption. 0.5 gm. charcoal and 50 cc. solution were used in the adsorption experiments and 0.3 gm. charcoal and 5 cc. solution for the swelling. The standing continued for 40 hours. The initial and final concentrations were titrated with N/5 barium hydroxide solution. The magnitude of the adsorption is expressed in Table X as the number of cubic centimeters of barium hydroxide. The height of the charcoal in air was indicated by h_0 and the height of the column in solution by h .

<u>Type of charcoal</u>	<u>Table X</u>			<u>Adsorbed by 1 gm. charcoal from 50 cc.</u>
	<u>h_0</u>	<u>h</u>	<u>$\frac{h - h_0}{h_0}$</u>	
1. Graphite, Kahlbaum preparation	7	7	0	1.2
2. Cane sugar charcoal, Kahlbaum	14	14.5	0.036	9.0
3. Animal charcoal, Kahlbaum	20	27	0.35	12.2
4. Animal charcoal A	35	43	0.214	12.2

Table X indicated a parallel between the value of the relative swelling and the adsorption value. Examination of Table X also showed that the height h_0 in air of equal weights of different types of charcoal is different. It was assumed that the quantity h_0 could be used as a sure indicator of the activity of a charcoal.

Summary

1. Charcoal swells in both pure solvents and solutions. The swelling isotherm in acetic acid solutions has minimum and maximum points.
2. Capability of swelling and adsorption capacity are closely connected.

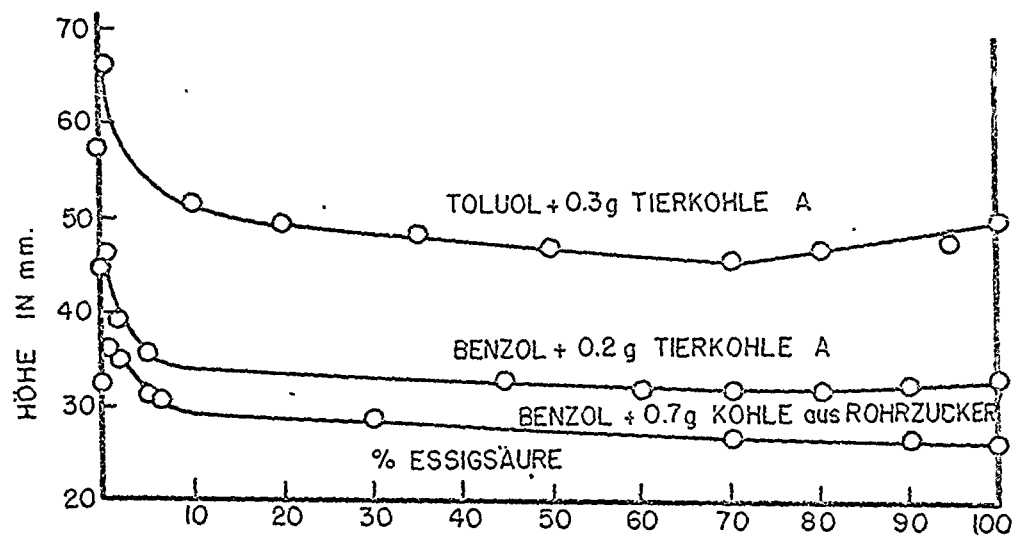


Fig. 1

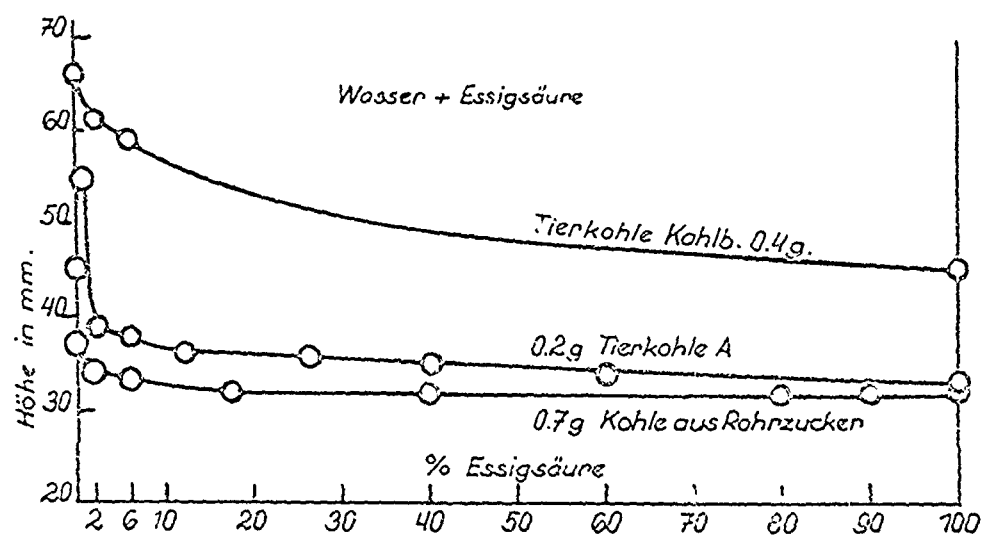


Fig. 2